BIOGAS REFORMATION OVER Pr-PROMOTED Ni/MgO

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ABSTRACT

Promoting rare earth element into commercial catalyst has become interesting research in designing the best catalyst for methane dry reforming. 1wt%, 3wt% and 5wt% Pr loadings into Ni/MgO were prepared by wet-impregnation method and calcined at 973 K. The prepared catalyst was characterized using N_2physisorption, field emission scanning electron microscopy (FESEM), X-ray diffraction spectroscopy (XRD) andenergy dispersive X-ray spectroscopy (EDX). The BET surface area increasedwhen the Pr loading percentage was increased. The surface area for 1wt% Pr loading of Pr-Ni/MgO was 14.3 m^2/g and 28.11 m^2/g for 5wt% Pr loading. The structure of the 5wt% Pr promoted Pr-Ni/MgO was much closely packed compared to the non-promoted Ni/MgO that captured by FESEM. Furthermore, XRD peak shows no peak of PrO for 5% Pr-Ni/MgO as the interaction was strong and well dispersed that didn't allow the XRD to detect. This statement was further supported by EDX result that showed the Pr was well dispersed on the catalyst. The MgO peak was found at 28.34º, 37.02º, 42.99º, 62.99º, 62.40º, 74.85º and 78.83º. Reaction studies over the Pr-Ni/MgO showed that the 5wt% promoted consistently yielded the best reaction at 1073, 1123 and 1173 K respectively. The conversion can reach ca. 61.44 % at 1173K when reactant volumetric flow ratio, CO_2/CH_4 was fixed at unity. In addition, the product H_2/CO ratioswere found to be less than 3.0 which were similar to the values reported in most of the other studies. The reaction power order for the CH_4 and CO_2 was 0.6111 and 0.4274 respectively whilstthe activation energy and activity for the reaction over 5wt% Pr-Ni/MgO catalyst was 66.10kJ/mol and 0.372.

Keywords: Catalyst, syngas, methane dry reforming, activation energy, activity

ABSTRAK

Penggalakkan unsur Nadir bumi ke dalam pemangkin komersial telah menjadi penyelidikan yang menarik dalam mereka bentuk pemangkin terbaik untuk reformasi kering metana. Promosi berat 1%, 3% dan 5% Pr ke dalam Ni/MgO telah disediakan mengunakan kaedah basah-impregnasi dan dikalsinasikan pada 973 K. Pemangkin yang disediakan, disifatkan menggunakan physisorpsi N_2, pelepasan bidang mengimbas microscopy elektron (FESEM), Spektroskopi belauan sinar-x (XRD) dan tenaga dispersive X-ray spektroskopi (EDX).). Luas permukaan BET meningkat apabila peratusan berat Pr yang dimuatkan meningkat. Luas permukaan untuk pemangkin yang dipromotkan 1% Pr-Ni/MgO ialah 14.3 m^2/g dan 28.11 m^2/g bagi 5% Pr-Ni/MgO. Struktur pemangkin 5% Pr dalam Pr-Ni/MgO dibandingkan dengan Ni/MgO yang tidak dipromotkan Pr adalah lebih rapat didapati dari FESEM. Selain itu, kemuncak XRD menunjukkan tiada puncak bagi PrO dalam 5% Pr-Ni/MgO kerana interaksi kuat terhadap pemangkin yang tidak membenarkan XRD untuk mengesan. Kenyataan ini seterusnya disokong oleh EDX yang menunjukkan Pr yang tersebar baik pada pemangkin. Puncak MgO didapati pada 28.34º, 37.02º, 42.99º, 62.99º, 62.40º, 74.85º dan 78.83º. Kajian tindak balas ke atas semua pemangkin Pr-Ni/MgO menunjukkan bahawa 5 % Pr yang dipromotkan kepada Pr-Ni/MgO memberi hasil tindak balas terbaik pada suhu 1073 K, 1123K dan 1173K. Penukaran methana mencapai 61.44% pada suhu 1173 K apabila nisbah aliran isipadu CO_2/CH_4 ditetapkan pada satu. Di samping itu, nisbah produk H_2/CO didapati kurang dari 3.0 yang mirip kepada nilai yang dilaporkan dalam kebanyakan kajian lain. Perintah kuasa reaksi untuk CH_4 dan CO_2 didapati 0.6111 dan 0.4274. Manakala tenaga pengaktifan dan aktiviti bagi tindak balas ke oleh pemangkin yang dipromotkan 5% Pr-Ni/MgO adalah 66.10 kJ/mol dan 0.372.

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Pr	: Praseodymium
C	: characteristic constant of the adsorbate
D	: inter plane distance of crystal
$d_{spacings}$	: interplanar distance
D	: crystalline size
Ea	: activation energy
k_{Sch}	: Scherrer constant
n	: order of reflection (integer)
P	: gas pressure
Ps	: saturation pressure of the adsorbate gas
P/Po	: relative pressure
r_k	: pore radius
R	: gas constant
T	: temperature
V	: volume of gas adsorbed
V_m	: volume of gas adsorbed corresponding to monolayer coverage
vm	: liquid molar volume
DRM	: Dry reforming of methane
POM	: Partial Oxidation of Methane
ppm	: Part per million

CHAPTER 1

INTRODUCTION

1.1 Introduction

Crude palm oil demand is growing tremendously in Malaysia and accounted as among the world largest palm oil producer. It is a well-known fact that palm oil has higher yield of production per hectare than the other oil seed crops including soybeans (Chin et al., 2013), hence its relatively lower price compared to the other oil and burgeoning demand. Although crude palm oil industry is expanding tremendously, it produces significant amount of palm oil mill effluent (POME) from crude palm oil mills. POME is acidic typified by its pH of 4 to 5 (Rupani et al., 2010). Significantly, POME degradation contributes to greenhouse gases such as CO_2, CH_4, NO_X, HFC, per-fluorocarbon and SF_6 which are detrimental to weather pattern (Kaewmai et al., 2012). Further studies also found that H_2S amount was very low (< 2000 ppm) while CH_4 (65%) and CO_2 (35%) constitute the highest proportion (Yacob et al., 2005). Therefore, POME treatment could be considered to become part of greenhouse effect contributor.

In the current practice, biogas is used as feed for electricity generation. However, the substantial amount of CO_2, which is a natural fire-repellent, decreases the efficiency of combustion (Yacob et al., 2005). Alternatively, biogas reformation reaction is proposed in the current work, which involves the reaction of CO_2 with CH_4 over specific catalysts. Significantly, there are three methods of reaction found in literature viz. steam reforming of methane (SRM), dry reforming of methane (DRM) and partial oxidation of methane (POM) (Meshkani et al., 2013). Biogas reformation is the reaction between CO_2 and CH_4 to produce synthesis gas (syngas), a mixture of CO and H_2 vital as an intermediate reactant for Fisher-Tropsch synthesis to produce liquid hydrocarbon. In order to fully utilize the biogas from POME, dry reforming of CH_4 (DRM) is a wise pathway as these two reactants are readily available as main components of biogas. Furthermore, Fisher-Tropsch synthesis requires H_2:CO composition of less than 3.0

(Meshkani et al., 2013). In some literatures, it were claimed that dry reforming of methane produced syngas with H_2:CO composition ratio that met the requirement (Meshkani et al., 2013). Basically, Ni, Pt, Rh and Ru exhibit good activity in dry reforming of methane (DRM) (Meshkani et al., 2013). However, those metal are expensive and rarely available. It is found that, ruthenium catalyst shows the best activity among other transition catalyst (Zhang et al., 2013). Although Ru is very good catalyst for reformation of CH_4, the price is not suitable for the industrial application. Thus, the researchers choose the cheapest metal and test them accordingly to obtain the best catalyst for the highest conversion of the biogas. Co, Ni and Fe were in the list of more economical catalysts. From literature, Ni found to give the highest conversion among three of the catalyst (Meshkani & Rezaei, 2011).

Therefore, Ni is selected as the suitable catalyst for biogas reformation. Dry reforming of methane is an endothermic reaction conducted with Ni catalyst to give high conversion of methane. However, the major drawback of this reaction is catalyst deactivation. Catalyst deactivations refer to the loss of catalytic activity or selectivity toward time. There are two major factors contribute to catalyst deactivation in this reaction which is by carbon deposition and/or sintering. Carbon deposition means, the carbon deposited onto the actives site of Ni and reduces the site for reaction on the catalyst. Sintering is the process of Ni growth in size that reduces the specific surface area of catalyst. Sintering mostly affected by the temperature of the reaction. Carbon deposition can occur either by methane cracking or carbon monoxide decomposition. These reactions produce solid carbon and deposited onto the actives site of the Ni catalyst. Since it is harder to control the reaction of carbon formation, catalyst support was introduced. Carbon deposition mostly favours acidic surface to accept electron and deposit onto the catalyst surface. Therefore, alkaline earth metal oxides were introduced to reduce the surface acidity of the catalyst and furthermore promoting electron species also included to retard the carbon formation. This study is about preparing Ni supported on magnesium oxide promoted by praseodymium oxide in dry reformation of biogas reaction.

1.2. Motivation

Since the crude palm oil (CPM) production increases every year, the more palm oil mill effluent (POME) being produced. Thus, it's indirectly increases the amount of biogas release to atmosphere while POME being treated. So, it is necessary to convert this gas into synthesis gas as way to curb excessive emission of greenhouse gases. As aforementioned, biogas reforming remains the only reaction that utilizes the entire biogas without a need to purify the biogas. Previously, many catalyst studies have been carried out to obtain the best reforming catalyst and mostly showed Ni as the best candidate although it was also found that it was prone to deactivation. Therefore, to mitigate this issue, alkaline earth metal oxide as support was employed. In some studies, Ni support limited to aluminium based. Therefore, to increase the basicity of the catalyst surface alkaline earth metal oxide like magnesium oxide with Praseodymium oxide promoter could be best choices in this study.

1.3. Objectives

This research is to prepare the Pr-Ni/MgO catalyst with different amount of praseodymium oxide and to study the biogas reforming performance.

1.4. Scope of study

To achieve the objectives, several tasks were carefully implemented:

I. Catalyst preparation and characterization

Catalyst preparation was a vital part of the research. Ni/MgO catalyst promoted with different amounts of Praseodymium oxide were prepared by impregnation method. Then, the catalyst were characterized using some equipment such as:

1. Brunauer – Emmett –Teller (BET)
2. X-ray Diffraction (XRD)
3. Field Emission Scanning Electron Microscopy (SEM)
4. Energy Dispersive X-ray (EDX)

II. Reaction

DRM was conducted in packed bed reactor at atmospheric pressure with different temperature and reactant flow ratio. Screening conducted at CO_2/CH_4 volumetric ratio of 1:1 at 1073K, 1123K, and 1173K. The reaction temperature selection for the best performed catalyst was chosen within the screening process.

Summary

Dry reforming methane is very essential to reduce the greenhouse effect that contributed by palm oil mill effluent decomposition. This reaction is the only reaction utilized the major product component from the POME decomposition. Choosing the best catalyst for this particular reaction must be precisely investigated with previous study. Ni metal is the best choice of active sites for industrial application purpose. Since introducing alkaline support could benefit the reaction stability. MgO chosen as the best choice of carrier for this particular catalyst. In order to increase further the reaction conversion of methane and the stability of the catalyst, Pr is promoted into the catalyst to study the activity of the catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Synthesis gas is a very crucial raw material for many downstream chemicals such as ammonia, methanol, dimethyl ether and most importantly the increasingly-demanded synthetic fuel by Fisher-Tropsch reaction plant (Aasberg-Petersen et al., 2011). POME upon decomposition would release abundant quantity of CH_4 and CO_2 with traces amount of H_2S (Yacob et al., 2005). Significantly, there are three routes of reaction to produce synthesis gas, viz. methane steam reforming, methane dry reforming and partial oxidation of methane (Meshkani et al., 2013). Methane steam reforming is the most commonly found reaction in many industries with the reaction as given by:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^0_{298} = 205.8 kJ mol^{-1} \tag{2.1}$$

As for more general hydrocarbon,

$$C_nH_m + nH_2O \leftrightarrow nCO + (n + \frac{1}{2}m)H_2 \quad \Delta H^0_{298} = 498.6\, kJ\, mol^{-1} (for\ C_3H_8) \tag{2.2}$$

Practically, methane steam reformation uses steam and methane as reactant to produce synthesis gas. This reaction is an endothermic reaction that requires external energy supply to conduct that particular reaction.

The second route of reaction is known as carbon dioxide reforming or methane dry reforming. This reaction uses CO_2 instead of steam to produce syngas. The reaction is given by

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = 247.0\, kJ\, mol^{-1} \tag{2.3}$$

Methane dry reformation is an endothermic reaction that uses CH_4 and CO_2 as the reaction feed. Unlike the two previous routes, partial oxidation is mildly exothermic reaction, which releases heat for each converted methane. The reaction equation given by,

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \qquad \Delta H_{298}^0 = -36.0\, kJ\, mol^{-1} \tag{2.4}$$

There are some studies that conduct combination of dry reforming of methane and partial oxidation (Meshkani et al., 2013). This would be very useful as the heat released from the partial oxidation can be utilized for the dry reforming of methane as it requires energy (Meshkani et al., 2013). Furthermore, this reaction can tune product gas flow rate ratio for H_2:CO to desirable ratio (Meshkani et al., 2013). However, to fully utilize the biogas, methane dry reforming could be the best choice as envisioned by the current study. In some literature also had stated that, the product gas flow rate ratio H_2: CO from dry reforming of methane is less than 3, which is suitable for Fisher-Tropsch synthesis.

2.2 Catalytic dry reforming of hydrocarbon

Dry reforming of methane is very appealing reaction that desires the industry to produce synthesis gas. It combines CH_4, which is the principal component of energy source, and CO_2 the greenhouse gas (Deutschmann, 2011). This reaction also very interesting as it uses methane and carbon dioxide, which is cheap feedstock that available abundantly from POME. Therefore, this is good alternative for steam reforming, which is used to produce synthesis gas. Furthermore, dry reforming of methane produces suitable product ratio of $H_2 : CO$ which is less than 3. This kind of product ratio is very suitable for Fischer-Tropsch synthesis of liquid hydrocarbon (Meshkani & Rezaei, 2011). In addition, the couple of dry reforming of methane and Fischer-Tropsch synthesis could be very useful as the heat from the Fischer-Tropsch reaction can drive the dry reformation of methane reaction to minimize the energy cost (Ni et al., 2013). Currently, many studies being conducted to improve this reaction by using catalyst. However, the major problem on the catalyst studies of this reaction is coking and sintering. One of the most recent studies is to avoid the coking by exploring the alkaline

earth metal oxide as the catalyst support for that particular reaction. In order to practically apply this reaction in industry, Ni catalyst was chosen as the catalyst. Ni catalyst is the best and cheap catalyst that is being used in recent industry to conduct dry reforming of methane.

The dry reforming of methane is given by,

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = 247.0\, kJ\, mol^{-1} \tag{2.5}$$

While carbon deposition may occur via, methane decomposition

$$CH_4 \rightarrow C(s) + 2H_2 \tag{2.6}$$

Or CO disproportionation (Boudouard) reaction,

$$2CO \leftrightarrow C + CO_2 \tag{2.7}$$

2.2.1 Kinetics

Kinetics study is very important to explain the nature of the reaction. Kinetics study is mainly function of support type, hydrocarbon nature and reaction condition (temperature and pressure) (Al-Ubaid, 1986). It is very expected that, methane dry reforming kinetics study being conducted extensively as it is cheap and abundantly available fuel gas from POME. A kinetic study on dry reforming of methane conducted by using $LaSrNiO_4$ (Pichas et al., 2010). In their study, the reaction temperature was conducted in range of 633K-713K at atmospheric pressure. Surface reaction between adsorbed methane and adsorbed carbon dioxide is considered as the rate determining steps. It was found that, the reaction order with respect to CH_4 be in range of 0.41– 0.89 and the reaction order respect to CO_2 found was approximately zero order. CH_4 conversion in this study found to be lower than carbon dioxide due to the water-gas shift reaction which given by,

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298} = 46.1 kJ / mol \tag{2.8}$$

There is another study on the kinetics using molybdenum carbide as alternatives catalyst for dry reforming of methane. (LaMont and Thomson, 2004) reported that was

successfully study the kinetics of molybdenum carbide in dry reforming of methane by stabilizing the Mo_2C catalyst by co-feeding CO with the reactant gases. They obtain the activation energy of 42.1 kcal/mol with reaction order of 1 respect to methane and 0.7 respect to carbon dioxide. (Darujati & Thomson, 2006) also further investigate the effect of promoting ceria on the aluminium oxide supported molybdenum carbide catalyst, . They found that, the reaction order of dry methane reforming is 0.95 ± 0.04 for methane and -0.18 ± 0.03 for carbon dioxide. This study conducted with partial pressure range of 0.02 to 0.24 bar for methane and 0.02-0.31 bar for carbon dioxide and the rest is supply by argon to maintain at atmospheric pressure. The activation energy obtained from this result was 45.5 ±0.99 kcal/mol. There are another studies were conducted on the bimetallic catalyst. (Özkara-Aydınoğlu & Erhan Aksoylu, 2013)Studied the kinetics of 0.2 wt.%Pt-15wt.%Ni/∂-Al_2O_3 and 0.3wt. %Pt-10wt% Ni/∂-Al_2O_3 .They found that the activation energy of 0.3% Pt promoted catalyst is 26.9 kcal/mol and 26.6 kcal/mol for 0.2 % Pt promoted catalyst. The reaction for 0.3 % platinum promoted Ni catalyst is 1 respect to methane and 0.87 for carbon dioxide. For the 0.2 % promoted platinum is 1.09 respect to methane and 1.40 for carbon dioxide. (Özkara-Aydınoğlu & Erhan Aksoylu, 2013) Mentioned that the reaction order for lower platinum content catalyst increases the carbon dioxide reaction order. This is because the oxygen in the carbon dioxide is utilized to clean the carbon deposit. Even there are many kinetic studies conducted over nickel based catalyst, there were some argument regarding the mechanism of the dry reforming reaction. The rate limiting step for dry reforming of methane is CH_xO decomposition. This rate determining step was concluded by (Leo et al., 2000) and (Osaki & Mori., 2001). There are other mechanism also proposed by (Bradford & Albert, 1996) and (Nandini et al., 2006) whereby involves dissociative CH_4 adsorption and CH_xO decomposition. Another study by (Aparicio, 1997) also reported that further dissociation of CH_4 and CO desorption as rate determination steps. From all this proposed rate determination steps, (Cui et al., 2007) concluded that the rate determining steps depend on their particular reaction temperature. Therefore, they study on typical $Ni/\alpha - Al_2O_3$ catalyst at temperature range of 823 to 1023 K to study the effect of temperature on the reforming reaction mechanism. They found that, CH_4 dissociation was the rate determining step and CO

desorption also was found to be limiting reaction in temperature range of 823-848 K. Table 2.0 show the literature studies on methane dry reforming with Ni catalyst.

Table 2.1: Kinetics from some previous study

Authors	Catalyst	Hydrocarbon	Kinetics order		Activation Energy	
			CH_4	CO_2		
(Pichas et al., 2010)	$LaSrNiO_4$	CH_4	0.41-0.89	~0	41.8	kJ/mol
(Darujati & Thomson, 2006)	30% Mo_2C/Al_2O_3(3 wt% Ce)	CH_4	0.95 ±0.04	0.18 ±0.03	45.5 ± 0.99	kcal/mol
(Özkara-Aydınoğlu & Erhan Aksoylu, 2013)	0.2%.Pt-15%Ni/Al_2O_3	CH_4	1.09	1.4	26.9	kcal/mol
(Özkara-Aydınoğlu & Erhan Aksoylu, 2013)	0.3%.Pt-10%Ni/Al_2O_3	CH_4	1	0.87	26.6	kcal/mol

2.2.2 Reaction Associated with Dry Reforming of Methane

It is very rare that any organic compound does not undergo any further side reaction. There are some reaction occur while the dry reforming reaction is conducted. The reaction could be in series reaction or parallel reaction. Dry reforming associated reaction is water gas shift reaction, Boudouard reaction and methane decomposition.

2.2.2.1 Boudouard Reaction

One of the side reactions is the Boudouard reaction which also known as CO disproportionation, where CO may dissociate to produce CO_2 and surface carbon as:

$$2CO \leftrightarrow C + CO_2 \qquad \Delta H^0_{298} = -172.5 kJ/mol \tag{2.9}$$

Thermodynamically, this reaction is likely to occur at a reaction temperature lower than 972 K. However, the presence of high concentrations of CO_2 in the system may facilitate keeping the influence of this reaction to a minimum. Also, quicker removal for CO from the system should assist in reducing the effect of this side reaction. Boudouard reaction mechanisms had been extensively studied by (Tottrup, 1976) And they found the reaction mechanism as follow:

$$CO + * \leftrightarrow CO* \tag{2.10}$$

$$CO* + * \rightarrow C* + O* \tag{2.11}$$

$$CO* + O* \leftrightarrow CO_2* \tag{2.12}$$

$$CO_2* \leftrightarrow CO_2 + * \tag{2.13}$$

Where, * symbolized as the actives sites of the catalyst, CO*, C*, O*and CO_2* is the chemisorb species on the catalyst. Carbon monoxide produced from the dry reforming reaction adsorbed onto the catalyst actives sites by single site adsorption. Then, the adsorbed carbon dioxide dissociates onto another sites of the catalyst form two site with carbon and oxygen. The chemisorbed oxygen will react with another carbon monoxide to become carbon dioxide while the carbon atom become deposited onto the catalyst surface and reduces the number of actives sites. This causes the catalyst activity reduces over time. (Tottrup, 1976) mention in his study that the carbon dioxide have influence

on the methane decomposition at temperature above 300 ^{o}C. However, methane dry reforming is endothermic reaction, which favor high reaction temperature. Thus, increasing the carbon dioxide amount in the feed could be very useful to reduce this reaction to occur. The rate of carbon monoxide decomposition (Boudouard reaction) is given by,

$$r = k\frac{p_{co}}{\left(1+K_A p_{co}+K_B\left(p_{co_2}/p_{co}\right)\right)^2} \tag{2.14}$$

Based on the rate law also can be concluded that, the rate of Boudouard reaction is directly proportional to the partial pressure of carbon monoxide. Therefore, removing the correct amount of carbon monoxide could benefit the catalyst stability. However, the CO removal amount should not affect the methane reforming reaction to shift to reactant as it reversible reaction.

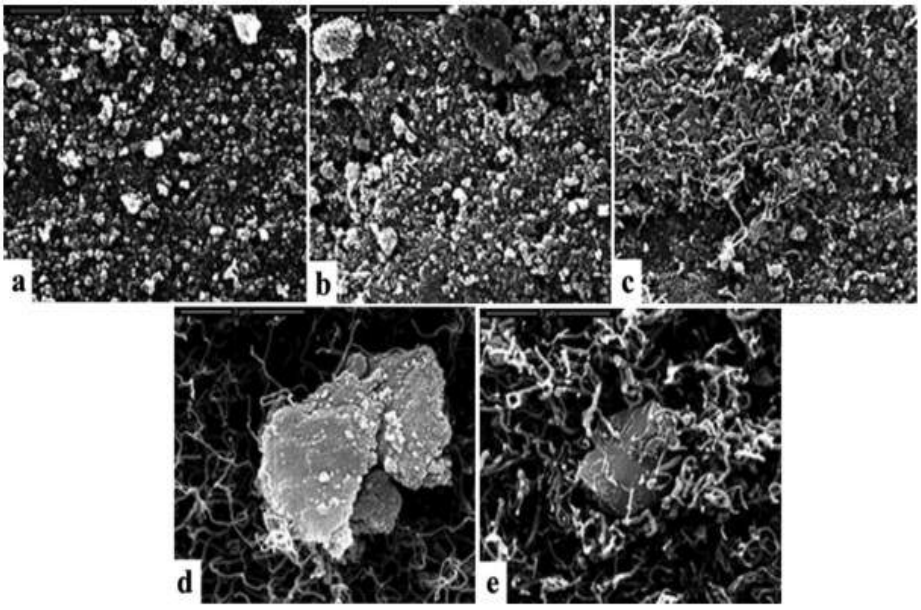

Figure 2.1: SEM images of Ni-Zr/SiO_2 catalysts after 10 h reaction at different temperature (a): 800 ^{o}C; (b): 750 ^{o}C; (c): 700 ^{o}C; (d): 650 ^{o}C; (e): 600 ^{o}C.

Figure 2.1 show an example of carbon deposition images of Ni-Zr/SiO_2 at different temperature. According to (Yao et al., 2013), at low temperature vermicular type carbon was observed and at high temperature, the vermicular carbon deposition was not found. This suggest that, the vermicular type carbon formation over this Ni-Zr/SiO_2 catalyst could be avoided if the reaction temperature is over 750 ^{o}C. This is one of the type of

carbon formation on Zr promoted catalyst. Each type of catalyst could give different structure of carbon deposition.

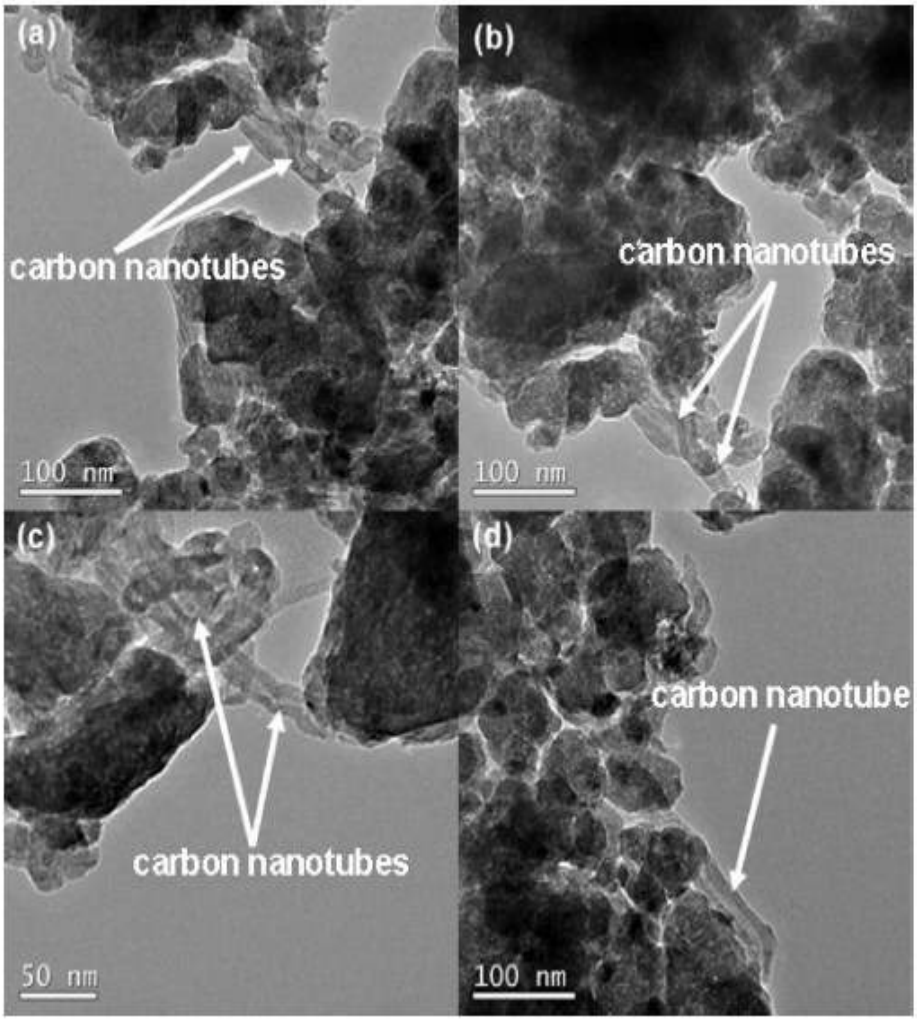

Figure 2.2: TEM images of the 50 h endurance-tested M-5Ni3Ce92Al catalyst

Figure 2.2 showing the TEM images on the carbon deposition mesoporous 3%Ce-5%Ni/92%Al studied by (Xu et al., 2013). Nano-tube carbon deposition type were found in their catalyst after 50 h in reaction. It was very interest also that, the carbon was distinctly distributed at different position on the catalyst. Furthermore, the images also shows the carbon deposition was not encapsulating the active Ni particle. As a result, the deactivation of the catalyst derived from the active site coverage was effectively avoided.

2.2.2.2 Reverse water gas shift reaction

Water gas shift reaction is commonly found reaction associated with dry methane reforming. Methane reforming produces hydrogen and carbon monoxide. Reverse water gas shift reaction occurs when hydrogen and carbon dioxide exist in the system. Therefore, this side reaction is series reaction to dry methane reforming. Water gas shift reaction equation is given by:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298} = 41\, kJ\, mol^{-1} \qquad (2.15)$$

There are specific studies have been conducted by (Azzam et al., 2008) on water gas shift reaction of propane dry reforming. They found that, water gas shift reaction occur in two reaction routes either by redox or associative formate mechanism. Redox mechanism involves successive reduction and oxidation of the catalyst support while associative mechanism involves reaction an adsorbed surface intermediates. Water gas shift reaction strongly dependent on the type of catalyst support. Principally, this reaction is very significant in a system containing a rich amount of CO_2 and H_2. It is slightly endothermic and is likely to take place at a higher temperature than 1073 K. likewise, prompt removal of H_2 or CO_2 from the system would lower the contribution of the RWGS reaction.

2.3 Previous Study on various catalyst for methane dry reforming

This section is generally studying various type of catalyst used in methane dry reforming. This studies could be divided into some of the fresh catalyst characterization studies, dry reforming reaction activity ad carbon deposition study.

Table 2.2: BET specific surface area from previous study

Catalyst	specific surface area, m^2/g	Reference	Calcined temperature, K	Preparation method
Co-CeO_2	25	(Luisetto, Tuti, and Di 2012)	823	Co-Precipitation method
Ni-CeO_2	22			

$Co\text{-}Ni/CeO_2$	26			
$14\%Ni\text{-}Al_2O_3$	209	(Castro Luna and Iriarte 2008)	1123	Sol gel
$14\%Ni\text{-}0.5\%K\text{-}Al_2O_3$	175			
$14\%Ni\text{-}0.5\%Ca\text{-}Al_2O_3$	192			
$14\%Ni\text{-}0.5\%Mn\text{-}Al_2O_3$	170			
$14\%Ni\text{-}0.5\%Sn\text{-}Al_2O_3$	179			
$5\%\ Ni/Al_2O_3$	173	(Alipour, Rezaei, and Meshkani 2013)	773	Wet impregnation method
$5\%\ Ni\text{-}3\%\ MgO/Al_2O_3$	155			
$5\%\ Ni\text{-}3\%\ CaO/Al_2O_3$	154			
$5\%\ Ni\text{-}3\%\ BaO/Al_2O_3$	169			
P123/Ni-MgO	115.9	(Zanganeh, Rezaei, and Zamaniyan 2014)	873	Surfactant assisted co-precipitation
P123/Ni-MgO	100.3		973	
P123/Ni-MgO	49.81		1073	
19% Ni/MgO	32	(Frusteri et al. 2001)	673	incipient wetness
1%K-18.7%Ni/MgO	24			
3%K-17.3%Ni/MgO	21			
$5\%Ni/La_2O_3$	15.2	(Ni et al. 2013)	1073	Co-precipitation
$5\%Ni/MgO\text{-}La_2O_3$	8.8			
$5\%Ni/3MgO\text{-}La_2O_3$	24.5			
$5\%Ni/5MgO\text{-}La_2O_3$	20.6			
$5\%Ni/10MgO\text{-}La_2O_3$	23.6			
$5\%Ni/20MgO\text{-}La_2O_3$	30.3			
5% Ni/MgO	63.1			

Table 2.2 show BET specific surface area of some catalyst for methane dry reforming by different type of preparation method. Regarding to the table 2.2, Al_2O_3 utilization as catalyst support, increase the surface area as it is mesoporous surface and help the active metal Ni to disperse onto the catalyst surface. As aforementioned, carbon deposition